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Published in:
Physical Review Letters

Link to article, DOI:
[10.1103/PhysRevLett.84.4898](https://doi.org/10.1103/PhysRevLett.84.4898)

Publication date:
2000

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):
Pedersen, M. Ø., Österlund, L., Mortensen, J. J., Mavrikakis, M., Hansen, L. B., Stensgaard, I., Lægsgaard, E., Nørskov, J. K., & Besenbacher, F. (2000). Diffusion of N adatoms on the Fe(100) surface. *Physical Review Letters*, 84(21), 4898-4901. <https://doi.org/10.1103/PhysRevLett.84.4898>

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Diffusion of N Adatoms on the Fe(100) Surface

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(Received 13 January 2000)

The diffusion of individual N adatoms on Fe(100) has been studied using scanning tunneling microscopy and *ab initio* density functional theory (DFT) calculations. The measured diffusion barrier for isolated N adatoms is $E_d = (0.92 \pm 0.04)$ eV, with a prefactor of $\nu_0 = 4.3 \times 10^{12} \text{ s}^{-1}$, which is in quantitative agreement with the DFT calculations. The diffusion is strongly coupled to lattice distortions, and, as a consequence, the presence of other N adatoms introduces an anisotropy in the diffusion. Based on experimentally determined values of the diffusion barriers and adsorbate-adsorbate interactions, the potential energy surface experienced by a N adatom is determined.

PACS numbers: 68.35.Fx, 61.16.Ch, 71.15.Mb

The diffusion of adsorbed atoms and molecules is one of the most fundamental processes on a solid surface. Adsorbate mobility is a crucial part of an atomic-scale description of a number of phenomena such as thin film growth, heterogeneous catalysis, corrosion, and sintering. However, very little is known about the details of the processes by which adsorbates move on a surface. In the past, information on diffusion of *gas species* has mainly been obtained from macroscopic diffusion experiments [1], in which the measured diffusion constant, derived through Fick's law, is in general an average over different diffusion processes. Recently, it has been demonstrated that microscopic information on surface diffusion of gas species can be obtained using scanning tunneling microscopy (STM) to track the position of individual adatoms on single crystal surfaces [2–5].

In this Letter, we show that an interplay between fast-scanning, atom-resolved STM imaging and *ab initio* density-functional theory (DFT) calculations leads to a consistent microscopic picture that explains from first principles the elementary diffusion events of adsorbed atoms on a metal surface. The diffusion barrier for isolated N adatoms on the Fe(100) surface is determined to be $E_d = (0.92 \pm 0.04)$ eV. From a detailed analysis we find that the diffusion barrier is significantly modified when neighboring adatoms are present. From DFT calculations the origin of the fairly large barrier is shown to be associated with a strong coupling between the N adatoms and the Fe lattice, leading to a large lattice strain at the transition state. These findings, together with information on adatom-adatom interactions [6,7], account quantitatively for the observed information on the anisotropy in the diffusivity, caused by the presence of neighboring N adatoms. Finally, it is shown how the potential energy surface (PES) experienced by a N adatom can be mapped out.

The experiments were performed in an ultrahigh vacuum chamber equipped with a home-built, fast-scanning, variable-temperature STM, capable of operating at tem-

peratures from 150 to 360 K [8]. The results were obtained on a 5000 Å thin Fe(100) single crystal, grown on a MgO substrate. The Fe crystal was cleaned by repeated cycles of Ar⁺ ion sputtering at 1.5 keV followed by annealing to 1000 K until the surface was clean and well ordered. The N atoms were deposited by thermal decomposition of NH₃ at 670 K. At this temperature NH₃ dissociates completely, and adsorption of H, NH, and NH₂ is eliminated. Exposures of 1.5–3 L NH₃ resulted in N coverages of $\Theta = 0.04$ –0.11, as determined by STM. After deposition the crystal was cooled and transferred to the STM. To avoid tip influence on the diffusion process, all of the STM images were recorded in the constant current mode at tunnel resistances $\geq 60 \text{ M}\Omega$ [9]. Series of time-lapse STM images were recorded using image recognition algorithms and active drift compensation to keep the same section of the surface in view. Such STM movies were recorded at different temperatures from 299 to 325 K, with an image rate varying from 6 to 30 frames/min.

A frame from an STM movie is shown in Fig. 1. Since N depletes the local density of states at the Fermi level, the N adatoms are imaged as depressions, in agreement with STM calculations [10]. From the atomically resolved STM images it is directly seen that the N atoms adsorb in fourfold hollow sites [11]. By tracking the motion of individual N atoms in these STM movies, the hopping rate and thus an energy barrier for diffusion E_d and the prefactor ν_0 can be extracted. We have studied both the diffusion of isolated N adatoms (separated by $>4a$ from the closest neighboring N adatom, where $a = 2.87 \text{ Å}$ is the Fe lattice constant) and the anisotropy in the diffusion introduced by neighboring N adatoms.

It is important to note that the observed displacements of the N atoms are not necessarily the same as the elementary jumps performed by the atoms. With a time separation between images comparable to the residence time of an adatom in a given site, it is possible for an adatom to perform more than one jump between two subsequent STM images. This effect can be included in the analysis using

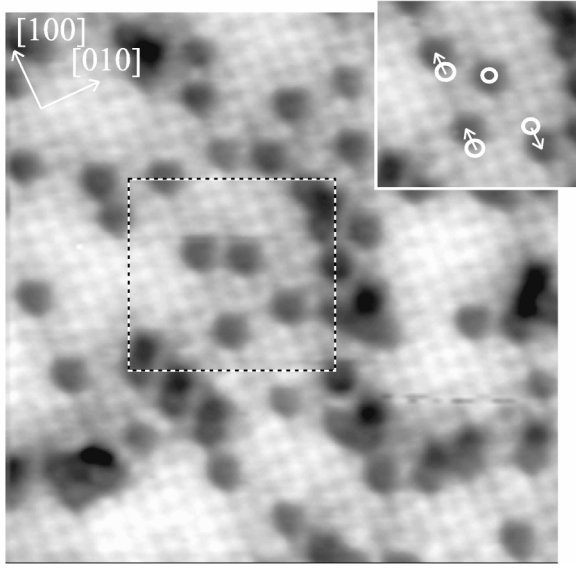


FIG. 1. STM image ($78 \times 76 \text{ \AA}^2$) obtained from an STM movie recorded at 300 K, tunneling parameters $V_t = -208.4 \text{ mV}$, $I_t = 1.21 \text{ nA}$. The inset shows an area marked by a dashed rectangle 62 sec later. Open circles in the inset mark the original positions of the four isolated N adatoms, and it can be seen that, in the intervening time, the N adatoms have performed one or more fundamental jumps.

elementary random walk theory [12]. The probability of finding a given adatom displaced by (i, j) lattice constants in the (x, y) plane after time T is given by

$$P_{(i,j)} = e^{-4h_0T} \times I_i(2h_0T) \times I_j(2h_0T). \quad (1)$$

Here $h_0 = h_x = h_y$ is the hopping rate, since a detailed statistical analysis using the formalism outlined by Ehrlich [12] shows that the diffusion is isotropic [13]; I_n is the modified Bessel function of the first kind. The hopping rate is determined from $P_{(0,0)}$ (the probability of observing the adatom in the same site in the following frame), which is given as $P_{(0,0)} = N/M$, where N is the number of observations where the atom apparently has *not* moved and M is the total number of observations. From the experimental value of $P_{(0,0)}$, h_0 can be deduced using Eq. (1). In Fig. 2 an Arrhenius plot of the hopping rate ($h_0 = \nu_0 e^{-E_d/k_B T}$) is shown, from which $E_d = (0.92 \pm 0.04) \text{ eV}$ is obtained with a prefactor of $\nu_0 = 4.3 \times 10^{12} \text{ s}^{-1}$, where the error bars are determined from the statistical spread $\sigma(P_{(0,0)}) = \sqrt{N(1 - N/M)/M}$.

To elucidate the physics behind the diffusion barrier we have performed DFT calculations using the procedure described in Ref. [14]. The Fe(100) surface is modeled by a three- or four-layer slab with a (2×4) or (2×5) periodicity parallel to the surface. The N atoms and the two topmost Fe layers in each configuration are allowed to relax completely. The large unit cells are necessary in order to minimize elastic interactions between the adsorbates in adjacent unit cells (see below). This approach gives an

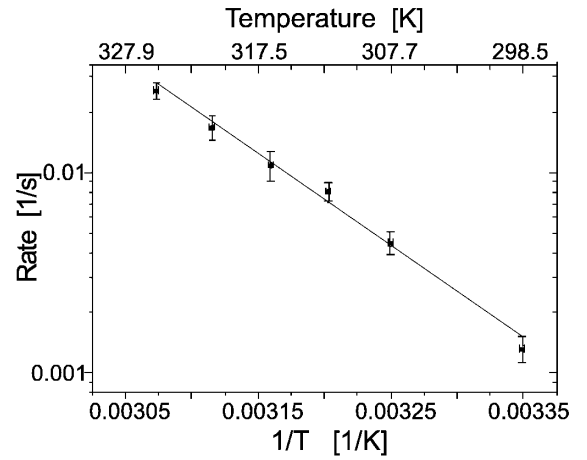


FIG. 2. Arrhenius plot of h_0 vs $1/T$. The straight line shows the least-squares best fit to the data points, resulting in $E_d = (0.92 \pm 0.04) \text{ eV}$ and $\nu_0 = 4.3 \times 10^{12} \text{ s}^{-1}$.

excellent description of the high coverage $c(2 \times 2)$ equilibrium structure and the bonding of N on Fe(100) [7].

We first determined the diffusion path for the three-layer thick slab using a (2×4) unit cell. In Fig. 3(a) the energy along the diffusion path is plotted as the N atom is displaced from one equilibrium fourfold position towards the neighboring fourfold position, with all other degrees of freedom being allowed to vary. It is seen that there is a small local minimum just at the midpoint where the N

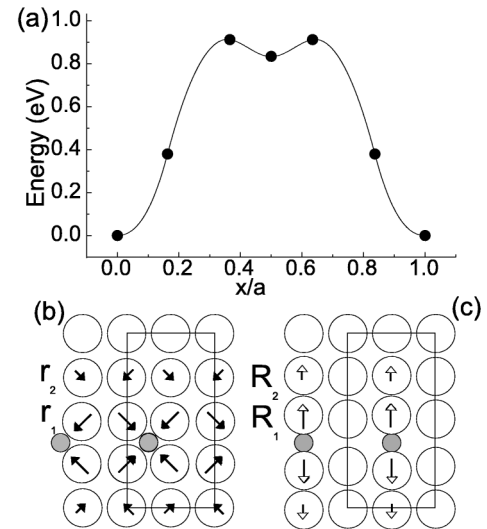


FIG. 3. (a) The total energy along a diffusion path leading from one fourfold hollow site to the neighboring site in a (2×4) unit cell in a three-layer slab. The energy of the maximum is 0.91 eV with a small metastable minimum at 0.83 eV. (b) The geometry used in (a) showing the N adatoms in the fourfold hollow site. (c) The calculated geometry in the metastable state. The calculated Fe atom displacements for a $p(2 \times 4)$ unit cell are $r_1 = 0.08 \text{ \AA}$ and $r_2 = 0.01 \text{ \AA}$ for the nearest-neighbor and the next-nearest-neighbor Fe atoms, respectively. The displacements at the transition state are $R_1 = 0.4 \text{ \AA}$ and $R_2 = 0.07 \text{ \AA}$, respectively.

atom is in the twofold coordinated site. The barrier for diffusion is found to be $E_d^{teo} = 0.91$ eV, while the energy of the metastable twofold site is 0.83 eV. As a control, the energy of the twofold site has been determined for a larger (2×5) unit cell with four layers, yielding 0.85 eV. For a fixed unit cell size, the difference in barrier height as the slab thickness is increased from 3 to 4 layers is 0.1 eV, which we suggest is the order of magnitude of the inherent accuracy of the calculated values arising from the model used to describe the surface. The value of the barrier does not depend on the exchange-correlation functional used (PW91 or RPBE [14]). We therefore conclude that the calculated diffusion barrier is in *quantitative* agreement with the measured value. In the following we will analyze the diffusion process in further detail.

Let us compare the calculated geometry in the fourfold site [Fig. 3(b)], and the geometry in the twofold site [Fig. 3(c)]. In the first site the N atoms give rise to a lateral *contraction* of the four nearest-neighbor Fe atoms by 0.06 Å towards the N atom, whereas in the twofold site the two nearest neighbor Fe atoms are pushed away from the N atom by almost 0.4 Å. The origin of the two effects is the same: the N adatoms seek a large metal coordination number. For this reason, the N distance above the surface is very small (only 0.3 Å), so that the N atom is coordinated to the Fe atom in the second layer, and the Fe atoms in the first layer are pulled towards the N atom. In the twofold site the N atom also stays deep in the surface to maintain coordination to the Fe atoms in the second layer. For the twofold site, this means that the two Fe atoms in the first layer are forced to move away due to Pauli repulsion. The huge local expansion of the Fe lattice at the (quasi)-transition state is the reason for the choice of a large unit cell. For a (2×2) unit cell the diffusion barrier is as high as 1.3 eV, because the freedom for the neighboring Fe atoms to relax is reduced. This shows that the coupling to the Fe lattice is an essential part of the diffusion process, and to describe the diffusion of individual adatoms we need to consider a large unit cell.

One consequence of the strong coupling between the (quasi)-transition state and the lattice is that the diffusion barrier should depend on the local surroundings, e.g., on the presence of neighboring N adatoms. Whereas isolated N adatoms diffuse with equal probability in any of the four possible directions, the presence of neighboring N adatoms is likely to introduce anisotropic diffusion. In order to quantify this effect experimentally, we have looked for situations where a diffusing N adatom has *one* neighbor within a radius of $r < 3a$ [marked "O" in Fig. 4(a)]. This rather large exclusion zone dramatically reduces the number of experimental observations and hence the statistics, but it is necessary to avoid interfering effects originating from interactions with a third adatom [6]. Figure 4(a) shows the number of observations (out of a total of 204) of each of the four possible elementary jumps that an adatom (labeled C) can perform, in the

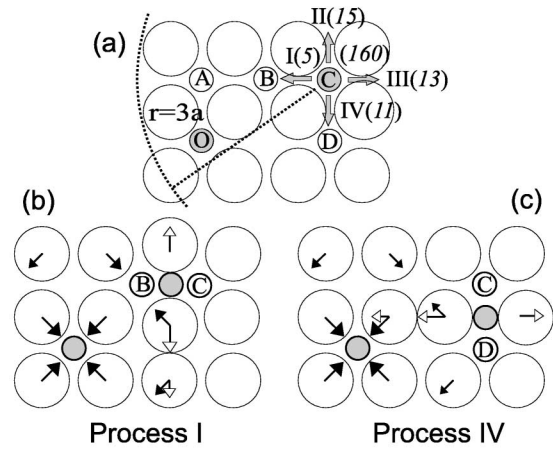


FIG. 4. (a) The number of jump events for an adatom located at site C, when another adatom is simultaneously resting at site O, as well as the number of observations where atom C did not move. To avoid the influence of interactions with a third adatom, an exclusion zone of $3a$ centered on the diffusing adatom was introduced in the analysis (indicated as a dashed arc centered on atom C). (b),(c) Schematic drawing of the displacement fields associated with a N adatom in the fourfold hollow site and at the transition states I (b) and IV (c), respectively.

presence of a resting N adatom at distance $r = \sqrt{5}a$ away. An approximate change in the barrier height (ΔE_x) can be deduced from $\Delta E_x = -k_B T \ln(h_x/h_0)$, where $x = \text{I, II, III, or IV}$ are the four possible jump directions indicated in Fig. 4(a). The diffusion barrier in direction I is significantly increased [$\Delta E_I = (29 \pm 15)$ meV], whereas the diffusion barriers in directions II, III, and IV are approximately unchanged within the accuracy of the measurements. As we will show below, the small increase of the barrier in direction IV [$\Delta E_{IV} = (6 \pm 11)$ meV] may be associated with a stiffening of the lattice due to the resting N adatom.

The interactions between the N adatoms, i.e., between one N atom in a fourfold site and another in a fourfold site or in the transition state, can be due to both electronic and lattice-mediated effects. The former dominates the interactions in sites A and B [6,7], but it cannot easily explain the increased barrier for process I, since here the adatoms move towards a site with a lower energy (cf. Fig. 5). The elastic interactions on the other hand easily explain the relative difference of the diffusion barriers, e.g., between processes I and IV. First, from Fig. 4(c) we note that the displacement field of the Fe atoms around the resting N adatom is in the same direction as the displacements of the Fe atoms caused by diffusion process IV, whereas it is found to be in the opposite direction to the displacement associated with diffusion process I, as depicted in Fig. 4(b). This is in quantitative agreement with the lower barrier for process IV compared to process I. Second, to explain the relative magnitude of process IV, which is in fact promoted by the displacement fields due to the resting N adatom [Fig. 4(b)], compared to processes II and III,

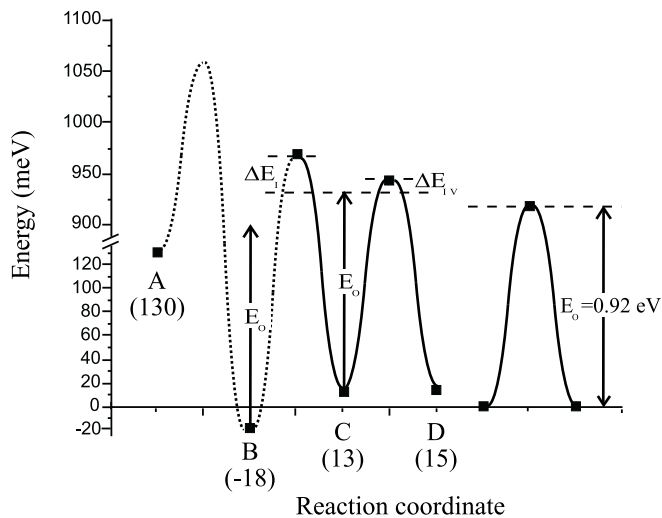


FIG. 5. The potential energy surface experienced by a N adatom when it is moved from site A to site D, when another N adatom is resting at site O [see Fig. 4(a)]. The dashed line between A and B indicates that it was not possible to measure the barrier height between these two sites with sufficient statistics. Interactions between the adatoms lead to shifts in the adsorption energies at sites A, B, C, and D (values in parentheses in meV) [6].

second order effects need to be considered. The resting N atom will tend to stiffen the lattice, causing a general increase in surface diffusion barriers for processes I and IV. Our DFT calculations show that N adsorption leads to an increase in the force constant by $\approx 40\%$ for the neighboring Fe atoms and hence an increased resistance to displacement. The magnitude of this stiffening causes the first and second order effects to be of the same order, and explains why process IV is equal, or even slightly suppressed, as compared to II and III.

Based on the above-mentioned analysis for all dimer configurations we can construct a potential energy surface for a N adatom in the vicinity of another N adatom. Figure 5 shows the PES for a N adatom along the path from sites A to D. In Fig. 5 the adsorption energy at sites A to D is drawn relative to an isolated N adatom, based on our previously determined values for the N-N interactions [6]. There are very few observations of the occupation of site A, which is consistent with a strongly repulsive nearest-neighbor interaction. Hence, information on the diffusion processes $A \leftrightarrow B$ is limited. Similarly, we find a relatively small number of jump events $B \rightarrow C$. This is in good agreement with an increased barrier for diffusion to site C. Moreover, an attractive next-nearest-neighbor interac-

tion implies an increased stability at site B, which in turn implies that there are only very few (5) observations of adatoms located in site B, with only one N adatom within a radius of $3a$. Instead, larger structures are formed [6].

In conclusion, we have measured the diffusion barrier for N adatoms on Fe(100) and found a barrier of $E_d = (0.92 \pm 0.04)$ eV. The microscopic origin of E_d is found to be due to the strain in the lattice in the transition state caused by a strong N-Fe coordination. The presence of neighboring N adatoms is found to lead to an anisotropy in the diffusion, which is explained by restrictions in the local expansion of the Fe lattice in the transition state. These quantitative results are of general interest also for other adsorbate systems, and the anisotropy provides a microscopic understanding of what can be interpreted as a concentration-dependent term in Fick's law for diffusion.

We acknowledge financial support from the Danish Natural Research Foundation through the Center for Atomic-Scale Materials Physics (CAMP), and from the Velux and the Knud Højgaard Foundations.

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